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**APPLICATION NUMBER: 60/561,623**

**FILING DATE: *April 12, 2004***

**RELATED PCT APPLICATION NUMBER: *PCT/US05/11705***



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## PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

INVENTOR(S)				
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)
Lori Ann Tina Marie		Stark-Kasley Leaym		Midland, Michigan 48642 Saginaw, Michigan 48603
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto				
TITLE OF THE INVENTION (280 characters max)				
Silsesquioxane Resin Wax				
Direct all correspondence to: CORRESPONDENCE ADDRESS				
<input checked="" type="checkbox"/> Customer Number		00137		Place Customer Number Bar Code Label here
OR		Type Customer Number here		
<input type="checkbox"/> Firm or Individual Name				
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ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification	Number of Pages	17	<input type="checkbox"/> CD(s), Number	
<input type="checkbox"/> Drawing(s)	Number of Sheets		<input checked="" type="checkbox"/> Other (specify)	Claims - 2 pages Abstract - 1 page
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76				
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)				
<input type="checkbox"/>	A check or money order is enclosed to cover the filing fees			FILING FEE AMOUNT (\$)
<input checked="" type="checkbox"/>	The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number			04-1520
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.				
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Respectfully submitted,

SIGNATURE



TYPED or PRINTED NAME Alan Zombeck

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Date

4/12/04

REGISTRATION NO.

45,260

(if appropriate)

Docket Number:

DC10047PSP1

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P19LARGE/REV05

**UNITED STATES PATENT APPLICATION  
FOR**

**Silsesquioxane Resin Wax**

5

Having the inventor(s):

Lori Ann Stark-Kasley

Tina Marie Leaym

10

**FIELD OF THE INVENTION**

[0001] The present invention relates to a silsesquioxane resin wax composition, methods for its preparation, and uses in personal, household, and medical care compositions. The silsesquioxane resin wax can be used in a variety of oil and gas field applications, such as for crude oil wax control.

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**BACKGROUND OF THE INVENTION**

[0002] Siloxane resins of the general formula  $R_nSiO_{(4-n)/2}$ , where R is an alkyl group and n is generally less than 1.8, are an important family of silicone polymers because of their utility in many commercial applications such as adhesive compositions and coatings applications.

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One particular subclass of siloxane resins, known as MQ resins (since they comprise primarily of "M" units of the general formula  $R_3SiO_{1/2}$  and "Q" units of the general formula  $SiO_2$ ), have found utility in cosmetic formulations. In particular MQ resins are commonly used in "extended wear" or "transfer resistant" cosmetic formulations. In these formulations, MQ resins enhance the substantivity of the pigments or other formulation actives to skin after application creating a longer lasting, and hence extended wear product.

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[0003] Representative examples of transfer resistant cosmetic compositions using MQ resins are found in US 6,071,503, US 6,074,654, US 6,139,823, US 6,340,466, WO 97/17058, and WO 97/17059 which disclose compositions comprising the combination of organosiloxane resins and fluid diorganosiloxane resins with a volatile carrier.

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[0004] Silsesquioxane resins of the general formula  $RSiO_{3/2}$  have also been used as additives in personal care formulations for a variety of functions. For example, in US Patent

5,733,537 by Halloran teaches the use of a non-polar silsesquioxane resin as a hair fixative. US Patent application publication 20030086888 by Legrow discloses trimethylsilylalkylsilsesquioxanes in leave-on compositions for personal care. More recently, US provisional applications 60/514,001 and 60/541,002, as filed by the same assignee as the present application, discloses MQ-propyl resins compositions and use in a variety of personal care formulations. Also, US provisional application 60/553,450, as filed by the same assignee as the present application, discloses alkyl-phenyl silsesquioxane resins in a variety of personal care applications.

[0005] While these references represent advances in the art, there is still a need for improved siloxane resins for use in skin care formulations that offer extended durability to cosmetic formulations, but also provide other functional benefits, such as moisturization, occlusivity, and improved feel. Furthermore, there is a need for siloxane resins having wax like characteristics, but yet still possess solubility in commonly used personal care solvents.

[0006] The present inventors have discovered improved siloxane resins by incorporating two distinct hydrocarbon groups in a silsesquioxane resin. The first hydrocarbon has 2 to 8 carbon atoms, and the second hydrocarbon group has 9 – 40 carbon atoms. The resulting siloxane resins, herein referred to as silsesquioxane resin wax, improve the substantivity of cosmetics after topical application to skin while also providing other functional benefits such as moisturization, occlusivity, and improved feel. The melting points and overall hydrocarbon content of the silsesquioxane resins can be adjusted to provide varying aesthetic benefits from a personal care formulation. The silsesquioxane resin wax can also be used in personal care formulations to improve fragrance retention and delivery of actives.

#### SUMMARY OF THE INVENTION

[0007] The present invention relates to a silsesquioxane resin wax comprising at least 40 mole % of siloxy units having the formula  $(R_2R'SiO_{1/2})_x(R''SiO_{3/2})_y$ , where x and y have a value of 0.05 to 0.95, R is an alkyl group having from 1 to 8 carbon atoms, an aryl group, a carbinol group, or an amino group, R' is a monovalent hydrocarbon having 9 – 40 carbon atoms, R'' is a monovalent hydrocarbon group having 2 to 8 carbon atoms.

[0008] The compositions of the present invention can be incorporated into a variety of personal, household, or medical care compositions. The silsesquioxane resin wax enhances

the durability and substantivity of cosmetics on skin after topical application from a formulation comprising the composition of the present invention. The silsesquioxane resin wax can also be used for crude wax control in oil and gas operations.

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### DETAILED DESCRIPTION OF THE INVENTION

[0009] The present invention relates to a silsesquioxane resin wax comprising at least 40 mole % of siloxy units having the formula  $(R_2R'SiO_{1/2})_x(R''SiO_{3/2})_y$ , where x and y have a value of 0.05 to 0.95, R is an alkyl group having from 1 to 8 carbon atoms, an aryl group, a carbinol group, or an amino group, R' is a monovalent hydrocarbon having 9 – 40 carbon atoms, R'' is a monovalent hydrocarbon group having 2 to 8 carbon atoms. As used herein, x and y represent the mole fraction of  $(R_2R'SiO_{1/2})$  and  $(R''SiO_{3/2})$  siloxy units relative to each other present in the silsesquioxane resin wax. Thus, the mole fraction of  $(R_2R'SiO_{1/2})$  and  $(R''SiO_{3/2})$  siloxy units each can independently vary from 0.05 to 0.95. Typically, the value of x is 0.05 to 0.95, or alternatively, 0.2 to 0.8, the value of y is 0.05 to 0.95, alternatively 0.2 to 0.8. However, the combination of  $(R_2R'SiO_{1/2})$  and  $(R''SiO_{3/2})$  siloxy units present must total at least 40 mole %, alternatively 60 mole %, or alternatively 90 mole % of all siloxy units present in the silsesquioxane resin wax. The silsesquioxane resin wax may be a liquid, soft solid, or solid material at room temperature.

[0010] The silsesquioxane resin wax can contain additional siloxy units such as (i)  $(R^1_3SiO_{1/2})_a$ , (ii)  $(R^2_2SiO_{2/2})_b$ , (iii)  $(R^3SiO_{3/2})_c$ , or (iv)  $(SiO_{4/2})_d$  units which are commonly known in the art, and also used herein, as M, D, T, and Q units respectively. The amount of each unit present in the silsesquioxane resin wax can be expressed as a mole fraction of the total number of moles of all siloxy units present in the silsesquioxane resin wax. Thus, the silsesquioxane resin wax of the present invention comprise the units:

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- (i)  $(R^1_3SiO_{1/2})_a$
- (ii)  $(R^2_2SiO_{2/2})_b$
- (iii)  $(R^3SiO_{3/2})_c$ ,
- (iv)  $(SiO_{4/2})_d$ ,
- (v)  $(R_2R'SiO_{1/2})_x$  and
- (vi)  $(R''SiO_{3/2})_y$ ,

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wherein

$R$ ,  $R^1$ ,  $R^2$ , and  $R^3$  are independently an alkyl group having from 1 to 8 carbon atoms,  
an aryl group, a carbinol group, or an amino group,

$R'$  is a monovalent hydrocarbon having 9 – 40 carbon atoms,

5  $R''$  is a monovalent hydrocarbon group having 2 to 8 carbon atoms,

$a$ ,  $b$ ,  $c$ , and  $d$  have value of zero to 0.6,

$x$  and  $y$  have a value of 0.05 to 0.95,

with the provisos that the value of  $x + y$  is equal to or greater than 0.40,

and the value of  $a + b + c + d + x + y = 1$ .

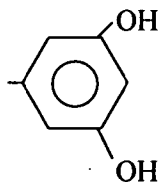
10 [0011]  $R'$  can be any linear or branched monovalent hydrocarbon having 9 to 40 carbons.

Alternatively,  $R'$  is a C18 – C40 hydrocarbon group.  $R''$  can be an ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or aryl group. Preferably,  $R''$  is propyl.

[0012] In one embodiment of the present invention, the selection of  $R'$  and the ratio of  $y/x$  is selected such that the silsesquioxane resin wax has a melting point greater than 30°C.

15 [0013] The  $R$ ,  $R^1$ ,  $R^2$ , and  $R^3$  in the units of the silsesquioxane resin wax are independently an alkyl group having from 1 to 8 carbon atoms, an aryl group, a carbinol group, an amino group, or a quaternary ammonium group. The alkyl groups are illustrated by methyl, ethyl, propyl, butyl, pentyl, hexyl, and octyl. The aryl groups are illustrated by phenyl, naphthyl, benzyl, tolyl, xylyl, xenyl, methylphenyl, 2-phenylethyl, 2-phenylpropyl ( $\alpha$ -methylstyrene)  
20 2-phenyl-2-methylethyl, chlorophenyl, bromophenyl and fluorophenyl with the aryl group typically being phenyl.

[0014] For the purposes of this invention a “carbinol group” is defined as any group containing at least one carbon-bonded hydroxyl (COH) radical. Thus the carbinol groups may contain more than one COH radical such as for example



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[0015] The carbinol group if free of aryl groups has at least 3 carbon atoms, or an aryl-containing carbinol group having at least 6 carbon atoms. The carbinol group free of aryl groups having at least 3 carbon atoms is illustrated by groups having the formula  $R^4OH$

wherein  $R^4$  is a divalent hydrocarbon radical having at least 3 carbon atoms or divalent hydrocarbonoxy radical having at least 3 carbon atoms. The group  $R^4$  is illustrated by alkylene radicals such as  $-(CH_2)_x-$  where x has a value of 3 to 10,

$-CH_2CH(CH_3)-$ ,  $-CH_2CH(CH_3)CH_2-$ ,  $-CH_2CH_2CH(CH_2CH_3)CH_2CH_2CH_2-$ , and

5  $-OCH(CH_3)(CH_2)_x-$  wherein x has a value of 1 to 10.

[0016] The aryl-containing carbinol group having at least 6 carbon atoms is illustrated

by groups having the formula  $R^5OH$  wherein  $R^5$  is an arylene radical such as

$-(CH_2)_xC_6H_4-$  wherein x has a value of 0 to 10,  $-CH_2CH(CH_3)(CH_2)_xC_6H_4-$  wherein x has a value of 0 to 10,  $-(CH_2)_xC_6H_4(CH_2)_x-$  wherein x has a value of 1 to 10. The aryl-

10 containing carbinol groups typically have from 6 to 14 atoms.

[0017] The amino group is illustrated by groups having the formula  $-R^6NH_2$  or  $-$

$R^6NHR^7NH_2$  wherein  $R^6$  is a divalent hydrocarbon radical having at least 2 carbon atoms

and  $R^7$  is a divalent hydrocarbon radical having at least 2 carbon atoms. The group  $R^6$  is typically an alkylene radical having from 2 to 20 carbon atoms.  $R^6$  is illustrated by ethylene,

15 propylene,  $-CH_2CHCH_3-$ , butylene,  $-CH_2CH(CH_3)CH_2-$ , pentamethylene, hexamethylene, 3-ethyl-hexamethylene, octamethylene, and decamethylene.

[0018]  $R^7$  is typically an alkylene radical having from 2 to 20 carbon atoms.  $R^7$  is

illustrated by ethylene, propylene,  $-CH_2CHCH_3-$ , butylene,  $-CH_2CH(CH_3)CH_2-$ , pentamethylene, hexamethylene, 3-ethyl-hexamethylene, octamethylene, and decamethylene.

20 [0019] Typical amino groups are  $-CH_2CH_2CH_2NH_2$  and

$-CH_2(CH_3)CHCH_2(H)NCH_3$ ,  $-CH_2CH_2NHCH_2CH_2NH_2$ ,  $-CH_2CH_2NH_2$ ,

$-CH_2CH_2NHCH_3$ ,  $-CH_2CH_2CH_2CH_2NH_2$ ,  $-(CH_2CH_2NH)_3H$ , and

$-CH_2CH_2NHCH_2CH_2NHC_4H_9$ .

[0020] Typically, R is a methyl group,  $R^1$  is a methyl group,  $R^2$  is a methyl or phenyl

25 group, and  $R^3$  is a methyl group.

[0021] Any individual D, T or Q siloxane units of the silsesquioxane resin wax can also

contain a hydroxy group and/or alkoxy group. Such siloxane units containing hydroxy and/or alkoxy groups are commonly found in siloxane resins having the general formula  $R_nSiO_{(4-n)/2}$ .

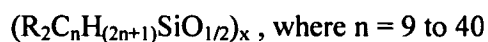


The hydroxy groups in these siloxane resins typically result from the reaction of the hydrolyzable group on the siloxane unit with water. The alkoxy groups result from partial hydrolysis when alkoxysilane precursors are used or from exchange of alcohol with hydrolysable groups. Typically, the weight percent of the total hydroxy groups present in the silsesquioxane resin wax is up to 10%. Typically, the weight percent of the total alkoxy groups present in silsesquioxane resin wax is up to 20 %.

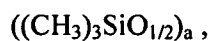
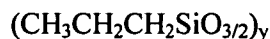
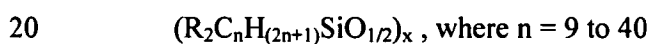
[0022] The molecular weights of the silsesquioxane resin wax are not restricted, but typically the number average molecular weight ( $M_N$ ) range from 1,000 to 10,000, or alternatively from 1,000 to 5,000.

10 [0023] The silsesquioxane resin wax of the present invention can be prepared by any of the methods known in the art for preparing siloxane resins having the general formula  $R_nSiO_{(4-n)/2}$  where R is an alkyl or aryl group and n is generally less than 1.8. Alternatively, the silsesquioxane resin wax can be prepared by the methods of the present invention as described infra.

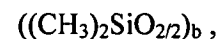
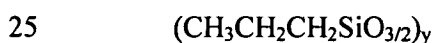
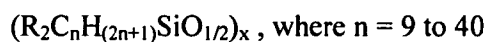
15 [0024] The silsesquioxane resin wax of this invention are illustrated by a silsesquioxane resin wax comprising the units;



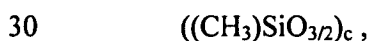
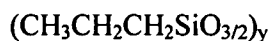
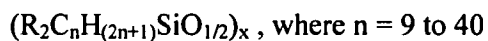
a silsesquioxane resin wax comprising the units;



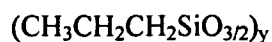
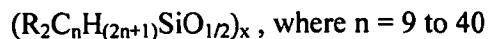
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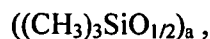
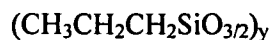
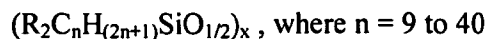
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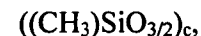
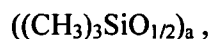
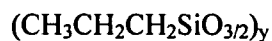
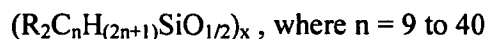
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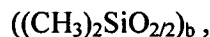
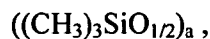
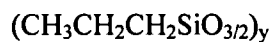
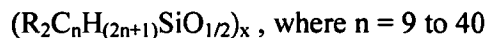
5 a silsesquioxane resin wax comprising the units;



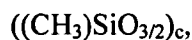
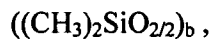
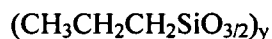
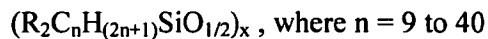
10 a silsesquioxane resin wax comprising the units;



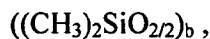
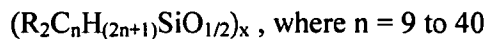
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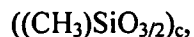
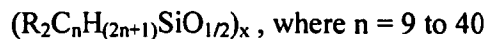
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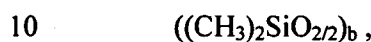
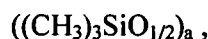
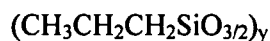
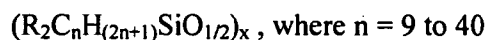
25 a silsesquioxane resin wax comprising the units;



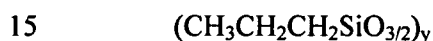
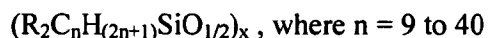
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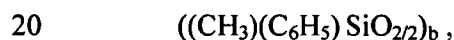
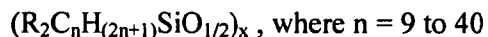
a silsesquioxane resin wax comprising the units;



a silsesquioxane resin wax comprising the units;



a silsesquioxane resin wax comprising the units;



wherein a, b, c, and d have value of zero to 0.4, x and y have a value of 0.05 to 0.95,

with the provisos that the value of x + y is equal to or greater than 0.40, and the value

of a + b + c + d + x + y = 1,

and R is equal to an alkyl group having from 1 to 8 carbon atoms, an aryl group, a carbinol

group, or an amino group.

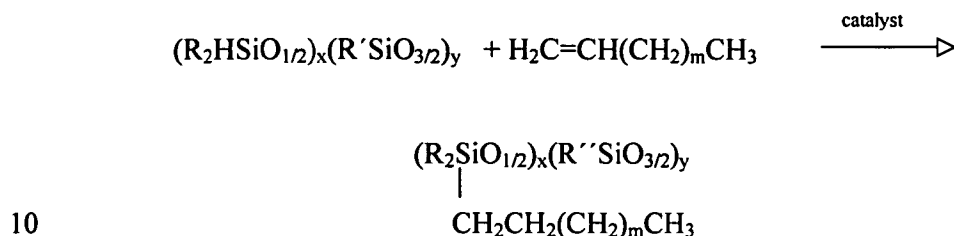
**[0025]** In all the formulas illustrated above, the R' group is designated as being on the M siloxy unit. In another embodiment of the present invention, the R' group can be on either a D or T siloxy unit.

**[0026]** The present invention also provides a method for preparing a silsesquioxane resin wax. The method comprises reacting;

A) a SiH containing alkyl silsesquioxane resin,

- B) a C<sub>9</sub> – C<sub>40</sub> vinyl terminated hydrocarbon,  
 C) a hydrosilylation catalyst, and optionally  
 D) a solvent.

5 [0027] The reaction is illustrated by the following general scheme;



where m = 6 – 37, and a, x, y, R, and R'' are as defined above.

[0028] Component A), the SiH containing alkyl silsesquioxane resin, can be prepared by  
 15 any of the methods known in the art to prepare such resins, but typically are prepared by one  
 of two techniques. In the first technique, an alkylsilane having three hydrolyzable groups  
 such as a halogen or alkoxy group present in the alkylsilane molecule is co-hydrolyzed with a  
 hydrogen containing silane or siloxane. For example, the SiH containing alkyl  
 silsesquioxane resins can be obtained by the acid catalyzed reaction of an  
 20 alkyltrialkoxysilane, such as propyltrimethoxysilane, with tetramethyldisiloxane. In the  
 second technique, an SiH containing silane or siloxane is equilibrated with a pre-formed alkyl  
 silsesquioxane resin. For example, tetramethyldisiloxane can be reacted with a propyl  
 silsesquioxane resin to yield a SiH containing propyl silsesquioxane resin.

[0029] The additional M, D, T, and Q units, as described supra, can be introduced into the  
 25 silsesquioxane resin wax by incorporating such units into the SiH containing alkyl  
 silsesquioxane resin precursor by reacting an additional organosilane(s), selected to produce  
 the desired siloxy unit in the resulting resin during the co-hydrolysis of the propylsilane and  
 SiH silane or siloxane. For example, reacting methoxytrimethylsilane,  
 dimethoxydimethylsilane, methoxytrimethylsilane, tetramethoxysilane (or alternatively the  
 30 corresponding ethoxy or chlorosilane of each) will respectively introduce a M, D, T, or Q unit  
 into the SiH containing alkyl silsesquioxane resin. The amount of these additional silanes

present in the co-hydrolysis reaction is selected to meet the mole fraction definitions, as described supra.

5 [0030] Alternatively, the SiH containing alkyl silsesquioxane resin can be prepared by reacting a preformed alkyl silsesquioxane, an SiH containing silane or siloxane, and other siloxanes containing various M, D, T, and Q units using any method in the art known to effect reaction of M, D, T, and Q siloxane units.

[0031] The SiH containing alkyl silsesquioxane resin is reacted with component B), a vinyl terminated hydrocarbon in the presence of a hydrosilylation catalyst. Typically, the vinyl terminated hydrocarbon has the formula  $H_2C=CH(CH_2)_mCH_3$ , where m is 6-37. The vinyl terminated hydrocarbons known as alpha olefins having 6 to 40 carbon atoms or blends there of can be used. The vinyl terminated hydrocarbons are illustrated by Amoco Chemical Company's Alpha-Olefin Products, Chevron Phillips Chemical Company Alpha olefin C<sub>20-24</sub>, C<sub>24-28</sub>, C<sub>26-28</sub>, C<sub>30+</sub>, C<sub>30+HA</sub>, and Mitsui Chemicals America, Inc Tafmer®, to name a few.

15 [0032] The amounts of vinyl terminated hydrocarbon and SiH containing alkyl silsesquioxane resin can vary, but typically a molar excess of the vinyl terminated hydrocarbon is used vs. the amount of the SiH containing alkyl silsesquioxane resin in the hydrosilylation reaction to ensure complete reaction of all SiH in the reaction. Alternatively the vinyl terminated hydrocarbon is used in a 30 %, or alternatively 10% molar excess vs. the amount of the SiH containing alkyl silsesquioxane resin

20 [0033] The hydrosilylation catalyst is illustrated by any metal-containing catalyst which facilitates the reaction of silicon-bonded hydrogen atoms of the SiH containing alkyl silsesquioxane resin with the terminal vinyl groups of the vinyl terminated hydrocarbon. The metals are illustrated by ruthenium, rhodium, palladium, osmium, iridium, or platinum.

[0034] The metal-containing catalyst is typically a platinum-containing catalyst since they are the most widely used and available and because they provide a more favorable effect for the compositions of this invention in terms of improved reaction rates. Platinum-containing catalysts can be a compound or complex of a platinum metal.

25 [0035] One type of typical platinum-containing catalyst in the compositions of this invention is the composition that is obtained when chloroplatinic acid is reacted with an aliphatically unsaturated organosilicon compound such as divinyltetramethyldisiloxane, because of its easy dispersibility in organosilicon systems.

30

[0036] Preferably the hydrosilylation catalyst is selected from chloroplatinic acid, alcohol modified chloroplatinic acids, olefin complexes of chloroplatinic acid, complexes of chloroplatinic acid and divinyltetramethyldisiloxane, fine platinum particles adsorbed on carbon carriers, platinum supported on metal oxide carriers such as  $\text{Pt}(\text{Al}_2\text{O}_3)$ , platinum black, platinum acetylacetonate, platinum(divinyltetramethyldisiloxane), platinous halides exemplified by  $\text{PtCl}_2$ ,  $\text{PtCl}_4$ ,  $\text{Pt}(\text{CN})_2$ , complexes of platinous halides with unsaturated compounds exemplified by ethylene, propylene, and organovinylsiloxanes, styrene hexamethyldiplatinum, and  $\text{RhCl}_3(\text{Bu}_2\text{S})_3$ .

[0037] The amount of hydrosilylation catalyst that is used is not narrowly limited as long as there is a sufficient amount to accelerate a reaction between the vinyl terminated hydrocarbon and the SiH containing alkyl silsesquioxane resin at room temperature or at temperatures above room temperature. The exact necessary amount of this catalyst will depend on the particular catalyst utilized and is not easily predictable. However, for platinum-containing catalysts the amount can be as low as one weight part of platinum for every one million weight parts of components the vinyl terminated hydrocarbon and the SiH containing alkyl silsesquioxane resin. The catalyst can be added at an amount 10 to 120 weight parts per one million parts of components the vinyl terminated hydrocarbon and the SiH containing alkyl silsesquioxane resin, but is typically added in an amount from 10 to 60 weight parts per one million parts of the vinyl terminated hydrocarbon and the SiH containing alkyl silsesquioxane resin.

[0038] The hydrosilylation reaction can be conducted neat or in the presence of D), a solvent. The solvent can be an alcohol such as methanol, ethanol, isopropanol, butanol, or n-propanol, a ketone such as acetone, methylethyl ketone, or methyl isobutyl ketone; an aromatic hydrocarbon such as benzene, toluene, or xylene; an aliphatic hydrocarbon such as heptane, hexane, or octane; a glycol ether such as propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, or ethylene glycol n-butyl ether, a halogenated hydrocarbon such as dichloromethane, 1,1,1-trichloroethane or methylene chloride, chloroform, dimethyl sulfoxide, dimethyl formamide, acetonitrile, tetrahydrofuran, white spirits, mineral spirits, or naphtha.

[0039] The amount of solvent can be up to 50 weight percent, but is typically from 20 to 50 weight percent, said weight percent being based on the total weight of components in the

hydrosilylation reaction. The solvent used during the hydrosilylation reaction can be subsequently removed from the resulting silsesquioxane resin wax by various known methods.

- [0040] The silsesquioxane resin wax are useful in a variety of personal or medical care compositions. The silsesquioxane resin wax can be used either neat, or dispersed in a carrier. Typically, the carrier is selected from a volatile siloxane or organic solvent. The volatile siloxane solvent can be a cyclic polysiloxane, a linear polysiloxane, low molecular weight silsesquioxanes or Q siloxane structures, such as TM<sub>3</sub> or M<sub>4</sub>Q, or mixtures of any of the above thereof. Some representative volatile linear polysiloxanes are hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, tetradecamethylhexasiloxane, and hexadecamethylheptasiloxane. Some representative volatile cyclic polysiloxanes are hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, and dodecamethylcyclohexasiloxane. The organic solvent can be an alcohol such as methanol, ethanol, isopropanol, butanol, or n-propanol, a ketone such as acetone, methylethyl ketone, or methyl isobutyl ketone; an aromatic hydrocarbon such as benzene, toluene, or xylene; an aliphatic hydrocarbon such as heptane, hexane, or octane; a glycol ether such as propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, or ethylene glycol n-butyl ether, an acetate, such as ethyl acetate or butyl acetate, a halogenated hydrocarbon such as dichloromethane, 1,1,1-trichloroethane or methylene chloride, chloroform, dimethyl sulfoxide, dimethyl formamide, acetonitrile, tetrahydrofuran, or an aliphatic hydrocarbon such as white spirits, mineral spirits, isododecane, heptane, hexane or naphtha. Typically, the carrier is decamethylcyclopentasiloxane or isododecane. The silsesquioxane resin wax can be a paste, soft solid or solid dispersion in a carrier also.
- [0041] The alkyl silsesquioxane resin wax can be used in antiperspirants, deodorants, skin creams, skin care lotions, moisturizers, facial treatments such as acne or wrinkle removers, personal and facial cleansers, sunscreens, make-ups, color cosmetics, foundations, blushes, lipsticks, lip balms, eyeliners, mascaras, and powders. Furthermore, it is anticipated that the compositions of the present invention can be combined with various other components to prepare the personal care or medical care products described infra. These components include additional surfactants, moisturizers, pigments, sunscreens, fragrances, emollients,

structurants, thickeners, conditioning agents, and actives such as vitamins, antioxidants and the like and amino silicones, commonly used to formulate such personal care and medical products.

- 5 [0042] The silsesquioxane resin waxes are particularly useful to enhance the durability and substantivity of cosmetics in topical formulations and can be used as structurants in cosmetics. They can also be used in household care items such as polishes, waxes, vinyl and leather treatments and in wax control in crude oil recovery.

### EXAMPLES

- 10 [0043] The following examples are presented to further illustrate the compositions and methods of this invention, but are not to be construed as limiting the invention. All parts and percentages in the examples are on a weight basis and all measurements were obtained at about 23°C, unless indicated to the contrary.

- 15 [0044] The representative silsesquioxane resin waxes (intermediates to prepare them) of these examples are described using the M, D, T, and Q designation for the siloxy units present in the resin. The superscripts further describe the alkyl substitute present on the siloxy unit. The superscripts used herein designate the following; Pr is  $\text{CH}_3\text{CH}_2\text{CH}_2-$ , H is hydrogen (as  $\equiv\text{SiH}$ ). The subscripts describe the mole fraction of the siloxy unit in the resin.

20 **Materials**

- T<sup>Pr</sup> RESIN = propyl silsesquioxane resin at 71.0 wt % in toluene. The propyl silsesquioxane resin (abbreviated herein as T<sup>Pr</sup>) has the formula  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SiO}_{3/2}$  with a  $M_N$  of 3500 and  
25 7 wt% of OH groups was prepared from the hydrolysis of propyl trichlorosilane.

C18 olefin represents;  $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_{15}\text{CH}_3$  1-octyldecene, was used as received from Chevron Phillips Chemical Company, 10001 Six Pines Drive, The Woodlands, TX 77380.

- 30 C20 – C24 olefin represents;  $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_{20-24}\text{CH}_3$  was used as received from Chevron Phillips Chemical Company, 10001 Six Pines Drive, The Woodlands, TX 77380.



C26 – C28 olefin represents;  $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_{26-28}\text{CH}_3$  was used as received from Chevron Phillips Chemical Company, 10001 Six Pines Drive, The Woodlands, TX 77380.

C30+ olefin represents; CAS # 260255-62-7, was used as received from Chevron Phillips Chemical Company, 10001 Six Pines Drive, The Woodlands, TX 77380.

### Example 1 (reference)

#### *Preparation of $\text{MM}^{\text{H}}\text{T}^{\text{Pr}}$ Resins from $\text{T}^{\text{Pr}}$ silsesquioxane resin*

[0045] A 3-neck reaction flask equipped with an agitator, temperature probe, Dean Stark trap and condenser was charged with a T propyl resin, hexamethyldisiloxane, tetramethyldihydrogendisiloxane and water at the ratios shown in Table 1. The Dean Stark trap was pre-loaded with toluene to insure the solids level was maintained. Trifluoromethanesulfonic acid was added as the catalyst at .01 wt% to the reaction mixture in the flask. The temperature of the reaction mixture was maintained at or below 50°C with a water bath initially as needed. When the temperature stabilized, the temperature was maintained at 50°C for 3 hours. Then, the reaction mixture was heated at reflux (100-140°C) and water removed via the Dean Stark trap as needed. After all the water formed in the reaction was removed, the resin mixture was allowed to cool and a 10x molar excess of calcium carbonate (9.31g to 700 microliters of FC-24) to neutralize the acid catalyst. The resin mixture was then filtered through a pressure filter and volatiles removed via a rotary evaporator.

**Table 1**

Example #	Wt% of $\text{T}^{\text{Pr}}$ Resin	Wt% of Hexamethyl disiloxane	Wt% of Tetramethyldihydrogendisiloxane	Ratio of $\text{Me}_3\text{Si}$ to $\text{Me}_2\text{HSi}$ disiloxane	Wt% of Water
1-1	77.4	16.5	1.5	90:10	4.6
1-2	78.3	9.3	7.7	50:50	4.7
1-3	79.6	0	15.6	0:100	4.8
1-4	77.6	14.7	3.1	80:20	4.6

**Example 2 (reference)***Preparation of MM<sup>H</sup>T<sup>Pr</sup> Resin from propyl trimethoxysilane*

[0046] A 3-neck reaction flask equipped with an agitator, temperature probe, addition  
 5 funnel and a condenser was charged with propyl trimethoxysilane, hexamethyldisiloxane,  
 tetramethyldihydrogendisiloxane and FC-24 catalyst at the ratios in Table 1. Water was then  
 added via the addition funnel. The temperature was maintained below 50°C by regulation of  
 water addition and use of water bath if needed. After the water addition, the temperature was  
 maintained 50°C for 3 hours. The resulting two phase reaction mixture was then placed in a  
 10 separatory funnel to separate the aqueous phase from the resin phase. Heptane was added in  
 sufficient amounts to help separate excess water from resin. The collected resin phase was  
 then put back in 3-neck flask and a 10x molar excess CaCO<sub>3</sub> was added to neutralize any  
 remaining acid catalyst. Water was also added to remove any methoxy present, and the  
 mixture heated to reflux (100-140°C) with a Dean Stark trap in place to remove trace  
 15 quantities of water and heptane. After cooling, MgSO<sub>4</sub> was added to remove any water that  
 is present. Finally, the resin was passed through a pressure filter.

**Table 2**

Example # Ratio of Me3 to Me2H	Wt% of Propyl trimethoxysilane	Wt% of Hexamethyl disiloxane	Wt% of Tetramethyl dihydrogen disiloxane	Wt% of FC-24	Wt% of Water
2-1 (0:100)	47.3	0	21.6	0.01	31.1
2-2 (50:50)	46.2	12.7	10.6	0.01	30.5

20

**Example 3***T<sup>Pr</sup> resin waxes from MM<sup>H</sup>T<sup>Pr</sup> resins*

25 [0047] This example describes the procedure used to prepare representative silsesquioxane  
 resin waxes of the present invention. The formulations used and description of the olefinic  
 wax is shown below in Table 3.

[0048] A 3-neck reaction flask equipped with an agitator, temperature probe, and a  
 condenser was charged with a siloxane resin (as prepared via reference example 1 or 2) and  
 30 sufficient heptane to reduce viscosity. The contents were then heated to 60-70°C. The  
 olefinic wax was then added to the reaction flask and followed by addition of the platinum

catalyst. After an initial exotherm, the temperature was maintained at 120° C for 3-4 hours and check Si-H of wax. The melt points of the resulting waxes were characterized by DSC, and shown in

Table 4 below.

5

**Table 3**

Example # (Resin Used, Wax used)	Wt% of T <sup>Pr</sup> Si-H Resin	Wt% of Wax	Wt% of Platinum Catalyst
1-1, C30+	91.72	8.28	0.02
1-1, C18	95.79	4.21	0.02
1-2, C30+	65.84	34.16	0.02
1-2, C18	79.85	20.15	0.02
1-3, C30+	46.84	53.16	0.02
1-3, C18	64.42	35.58	0.02
2-1, C20-24	31.67	68.53	0.02
2-1, C26-28	24.73	75.27	0.02
2-1, C30+	21.33	78.67	0.02

10

**Table 4**

Example #	Melt Point, °C
1-1, C30+	6, 44
1-1, C18	-63
1-2, C30+	34, 45
1-2, C18	-46,-11
1-3, C30+	NA
1-3, C18	56
2-1, C20-24	34
2-1, C26-28	56
2-1, C30+	66

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**Skin Moisturizer**

- 5 [0049] Procedure:  
Melt wax in DC 245, add hot mixture to DC 5225C while mixing with dual blade. Mix until dispersed. Increase mixing speed to 1376 RPM while adding water phase(water, NaCl and glycerin). Add water phase over 10 minutes. Mix for an additional 10 minutes.

10

Formulation for Skin Moisturizer

Material	Wt%
Oil Phase	
DC 245	10.0
DC 5225C	10.0
Silsesquioxane resin wax	2.0
Fragrance	0.5
Water Phase	
Glycerin	5.0
NaCl	1.0
DI Water	72.5

## CLAIMS

1. A silsesquioxane resin wax comprising at least 40 mole % of siloxy units having the formula  $(R_2R'SiO_{1/2})_x(R''SiO_{3/2})_y$ , where x and y have a value of 0.05 to 0.95, R is an alkyl group having from 1 to 8 carbon atoms, an aryl group, a carbinol group, or an amino group, R' is a monovalent hydrocarbon having 9 – 40 carbon atoms, and R'' is a monovalent hydrocarbon group having 2 to 8 carbon atoms.

2. The composition of claim 1 wherein the silsesquioxane resin wax comprises the units:

- (i)  $(R^1_3SiO_{1/2})_a$
- (ii)  $(R^2_2SiO_{2/2})_b$
- (iii)  $(R^3SiO_{3/2})_c$ ,
- (iv)  $(SiO_{4/2})_d$ ,
- (v)  $(R_2R'SiO_{1/2})_x$  and
- (vi)  $(R''SiO_{3/2})_y$ ,

wherein

R,  $R^1$ ,  $R^2$ , and  $R^3$  are independently an alkyl group having from 1 to 8 carbon atoms, an aryl group, a carbinol group, or an amino group,  
 R' is a monovalent hydrocarbon having 9 – 40 carbon atoms,  
 R'' is a monovalent hydrocarbon group having 2 to 8 carbon atoms,  
 a, b, c, and d have value of zero to 0.4,  
 x and y have a value of 0.05 to 0.95,  
 with the provisos that the value of x + y is equal to or greater than 0.40,  
 and the value of a + b + c + d + x + y = 1.

25

3. The silsesquioxane resin wax of claim 1 further comprising;  
 (C) a carrier selected from a volatile siloxane or organic solvent.

30

4. A personal care product comprising the silsesquioxane resin wax of claim 1 or 3.

5. The personal care product of claim 4, where the personal care product is a moisturizing cream or lotion.
6. A household care product comprising the silsesquioxane resin wax of claim 1 or 3.
- 5 7. A crude oil wax control product comprising the silsesquioxane resin wax of claim 1 or 3.
8. A process for preparing a silsesquioxane resin wax comprising reacting;
- 10       A) a SiH containing alkyl silsesquioxane resin,  
       B) a C<sub>9</sub>–C<sub>40</sub> vinyl terminated hydrocarbon,  
       C) a hydrosilylation catalyst,  
       and optionally,  
       D) a solvent.
- 15 9. The process of claim 8 where the SiH containing alkyl silsesquioxane resin comprises siloxy units of the formula  $(R_2HSiO_{1/2})_x(R'SiO_{3/2})_y$ , where
- R is an alkyl group having from 1 to 8 carbon atoms,  
          an aryl group, a carbinol group, or an amino group,  
       R' is a monovalent hydrocarbon group having 2 to 8 carbon atoms,
- 20       x and y have a value of 0.05 to 0.95,  
          with the provisos that the value of x + y in the SiH containing alkyl  
          silsesquioxane resin is equal to or greater than 0.40.

**ABSTRACT**

[0050] A silsesquioxane resin wax composition, method for its preparation, and use in personal, household, and medical care compositions are disclosed. The silsesquioxane resin  
5 wax can also find utility in a variety of oil and gas field applications, such as for crude oil wax control.